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Variation of kerogen content and mineralogy in some Australian tertiary oil shales

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ABSTRACT

Oil shale is a potential alternative source of petroleum products. The processes of retorting oil shale and refining shale oil are both affected by the composition of the parent rock. Mineralogical and geochemical data obtained from two bore holes in Queensland oil shale deposits are presented and discussed here. The data includes the variation with depth of mineralogy, ash content, moisture content and kerogen content. A strong correlation of hydrogen and organic carbon, and higher H/C ratios suggest that organic matter is present mainly as aliphatic compounds. Pyrite was identified as the major source of sulphur. This may provide some possibilities for easier removal of sulphur before the oil shale is processed.

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1. Introduction

Oil shale is a sedimentary rock that consists of a considerably large amount of organic matter called kerogen. Kerogen is a complex macromolecular organic structure, composed mainly of carbon, hydrogen and oxygen with minor amounts of nitrogen and sulphur. Hydrocarbons are released as vapour when kerogen is subjected to a temperature between 300 and 660° C in the absence of oxygen [1].

Tertiary oil shales in Queensland, Australia are a potentially valuable source of petroleum. It was estimated that the oil shales in ten deposits along the coast of central Queensland contain about 17.3 billion barrels of oil [2]. While most of the economically valuable Australian oil shales were formed during Tertiary, at least one deposit, namely Julia Creek deposit, was formed during Cretaceous period. Following table (Table 1) summarises the major Australian oil shale deposits.

A brief summary of other oil shale deposits around the world is given here for comparison with a special reference to Tertiary deposits.

Tertiary oil shales in other countries

Brazil has a lacustrine tertiary oil shale deposit in Paraiba Valley. This deposit has estimated resources of 2 billion barrels. In China Fushun and Maoming oil shale deposits are mainly of Tertiary age. It is estimated that Fushun has a total of 3,600 million tons of oil shale resource while Maoming is estimated at 5 billion tons [3]. Estonia's oil shale deposits are largely Palaeozoic. Total reserve of oil shale is estimated at 9.94 billion tons [4].

Israel has about 10 major deposits which are largely Cretaceous age. Jordan has over 5,200 million tons of oil shale which are late Cretaceous to early Tertiary in age. Neighbouring Syria also has considerable amount of oil shale deposits, some of which are considered to be part of the Jordanian deposits. Morocco has about ten oil shale deposits all of which are late Cretaceous in age. Russia has estimated reserves over 100 billion tons of oil shale, but some of these are notably high in sulphur (4–6%). Thailand has tertiary oil shale deposits of over 18.7 billion tons. Their sulphur content is approximately 1% [3].

A number of oil shale deposits are found in the United States and the ages of these deposits range from Precambrian to Tertiary. The Green River formation is one of the largest tertiary oil shale deposits. It is estimated that Colorado deposits contain about 131 billion tons of oil shale with the potential to produce over 1.0 trillion barrels while those in the Green River Basin in southwest Wyoming have about 35 billion tons of oil shale. In addition to these Tertiary deposits, the US has oil shale deposits of Devonian and older [3].

Turkey is estimated to have about 284 million tons of oil shale of Tertiary age. Canada and Sweden have oil shale deposits which are much older than Tertiary [3]. Armenia has relatively smaller tertiary oil shale deposits [5].

The composition of the shale oil, especially the amount of sulphur, nitrogen and other impurities, is an important factor in

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Table 1
Tertiary oil shale deposits in Queensland, Australia

Deposit	*In situ* oil 10^6 tons	Yield L/t	Area, km^2	Recoverable oil	
				10^6 m^3	10^6 bbls
Alpha	17	200+	10	13	80
Condor	17,000	65	60	1100	6700
Duaringa	10,000	82	720	590	3700
Lowmead	1800	84	25	120	740
Nagoorin	6300	90	24	420	2700
Nagoorin South	1300	78	18	74	470
Rundle	5000	105	25	420	2700
Stuart	5200	94	32	400	2500
Yaamba	6100	95	32	440	2800
Julia Creek[a]	4000	70	250	270	1700

From Dyni [3].

[a] Julia Creek deposits are supposedly older than Tertiary (Cretaceous), but are included here for the purpose of comparison.

determining the economic value of the oil shale. Regtop et al. [6] first studied the differences in shale oil from the Rundle oil shale deposit in Queensland. Of the seven seams in this deposit, they focussed their attention mainly on the Kerosene Creek and Ramsay Crossing seams. Results indicate that the compositions of the shale oil of Kerosene Creek and Ramsay Crossing are significantly different; for example, atomic H/C ratios for these were 1.6 & 1.7 respectively. Also, the proportion of total nitrogen content in each fraction was different.

Depending on the composition and the type of hydrocarbon in the shale oil, the refining processes must be adjusted accordingly, which influences the price of the final product. The composition of the shale oil depends on the composition of the parent rock, i.e. the oil shale. For example, high sulphur content in oil shale may produce "sour" oil which needs extensive processing to remove the sulphur in order to reduce SO_2 emission, which is an environmental concern.

It is therefore important to study the composition of the oil shale in detail, and understand the general trends in compositional variations and their implications. This paper aims to summarise the composition of some tertiary oil shale samples from Queensland, Australia. Previous researchers have addressed some of the geological and geochemical issues of these materials [7–10].

The mineralogical composition of oil shale can vary considerably between deposits and also within the deposit. The economic value of oil shale is totally dependant on the amount of oil that can be extracted from the rock, the environmental effects of extraction and the cost-effectiveness of the oil extraction. Although the amounts of available oil are largely dependent on the amount of kerogen in the rocks, they are also controlled by the mineralogy [11]. For example, certain minerals are known to have inhibitory or catalytic effects on kerogen-releasing reactions [12]. Therefore it is important to know the mineralogy of oil shale rocks that are used in retorting.

Many researchers have studied the mineralogy of selected oil shale samples as well as the effect of minerals on the retorting [13–18]. It is important to have a good understanding of the source rock and its mineralogy in order to design the best retorting conditions, as well as to predict the composition of the end products.

It is known that certain clay minerals can have an authigenic origin, i.e. formed as a result of a weathering process, while some are detrital or allogenic [19]. Chlorite, kaolinite, illite and some smectite types mostly exist as authigenic clays, while some quartz are common as allogenic minerals.

If the clays are authigenic, a decreasing trend with the depth should be expected because generally weathering occurs from top to bottom (unless it is a hydrothermal weathering). Also, easily altered minerals like feldspars should display an increasing trend with the depth. One of the objectives of this work is to determine if the oil shales have been subjected to weathering.

2. Material and methods

Bore hole data was obtained from South Pacific Petroleum Inc. Samples were collected from the boreholes by drilling vertically. Logged samples were arranged according to the depth and subsamples were obtained from these for various analyses. These samples were collected and prepared by the company that processes the oil shale, and extensive details on the samples and their locations withheld. Generally, all the samples were fine grained, relatively homogeneous rocks.

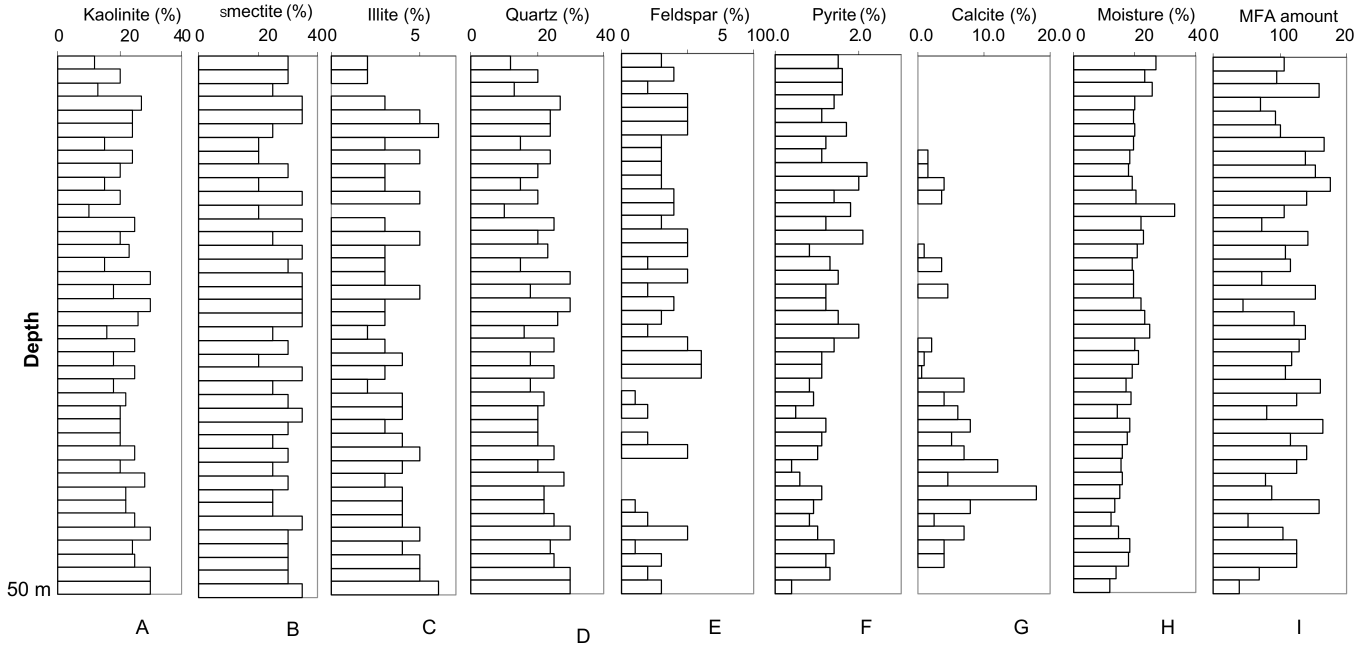

Fig. 1. Variation of different minerals, MFA values and moisture content with depth from the surface.

2.1. Mineralogical and elemental analyses

Samples were analysed for mineralogical composition. The analytical methods are not mentioned here, since the results contained herein come from the Elelmentar™ analytical company.

3. Results and discussion

The results (Fig. 1A–C) show that there is no clear trend in clay contents (separately or altogether) with the depth. This is a clear indication that the clays are primary and are of detrital origin. The random variation of quartz with depth also indicates that the clay minerals were deposited or formed together with quartz (Fig. 1D).

Feldspar and calcite are weathered relatively easily under meteoric weathering conditions. Meteoric weathering may add more moisture to the top of the deposit. As shown in Fig. 1E, G and H, moisture content as well as feldspar and calcite contents do not show a simple correlation with the depth. Therefore, it can be safely concluded that the samples used for the analyses were not exposed to meteoric weathering.

Fig. 2 shows that organic carbon and hydrogen are strongly correlated with each other and the average H/C atomic ratio is approximately 2.46. The high H/C ratio indicates that the hydrocarbons exist in a predominantly aliphatic form in the rocks. Hydrogen and Modified Fisher Assay (MFA) content are also strongly correlated, indicating that hydrogen is mainly in the form of kerogen. However, the organic carbon content shows some deviations from this trend (Fig. 2). This is also reflected in Fig. 3H versus organic C. This may be due to the presence of coal or other forms of organic carbons which are not converted into oil under standard MFA processing conditions. This explains the higher H/C ratio observed in this study compared to the results of Regtop et al. [6].

Fig. 4 indicates that there is a visible negative trend between quartz and MFA content. Generally, when the kerogen content is high, mineral (including clay) content is relatively low and vice versa, since kerogen and minerals are the major constituents that make up oil shale. Therefore, kerogen content has a negative relationship with total mineral content (see Fig. 5). Since ash is produced by the remaining minerals after kerogen removal, kerogen content (as well as MFA) has a negative relationship with ash (as well as clay mineral) content.

As shown in Fig. 6, SiO_2 content generally has a positive correlation with Al_2O_3 and iron oxides. This is mainly because of the presence of clay minerals. Clays are the major ferro-alumino silicates detected in oil shales from this region [6]. In addition, minor amounts of mica and feldspars also contribute to this trend. Any deviation from this trend is explained by the presence of silica

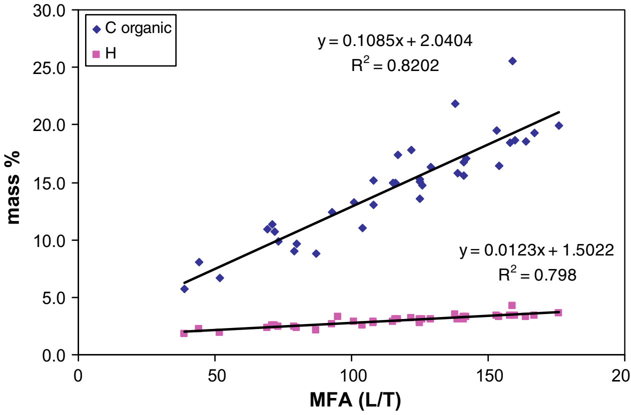

Fig. 2. Correlation of organic carbon and hydrogen with kerogen (presented as MFA) content. Note the strong correlation of hydrogen (H) & kerogen indicating that most of the hydrogen is coming from kerogen. Most of the samples show a strong positive correlation of organic carbon with MFA values as well.

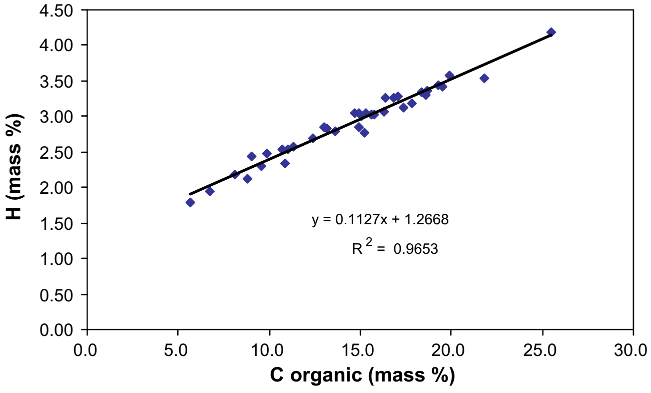

Fig. 3. Correlation of organic carbon with hydrogen. The strong correlation of H & organic carbon indicates that almost all organic carbon and hydrogen are in hydrocarbon form (i.e. in kerogen).

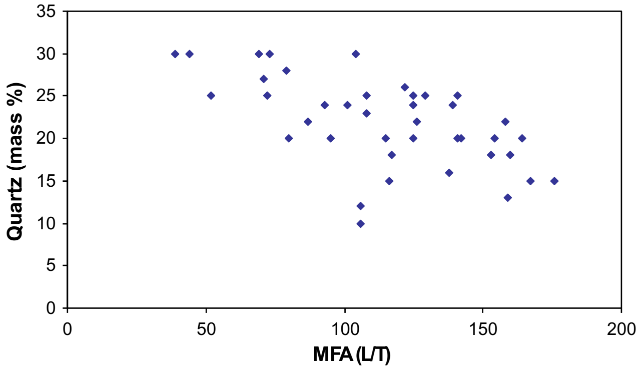

Fig. 4. Variation of MFA values and quartz contents. Quartz content has no direct relationship with MFA values. However, a weak negative correlation is visible due to the fact that quartz is the most abundant mineral and the increase of quartz percentage naturally decreases the other components' percentages, including that of kerogen.

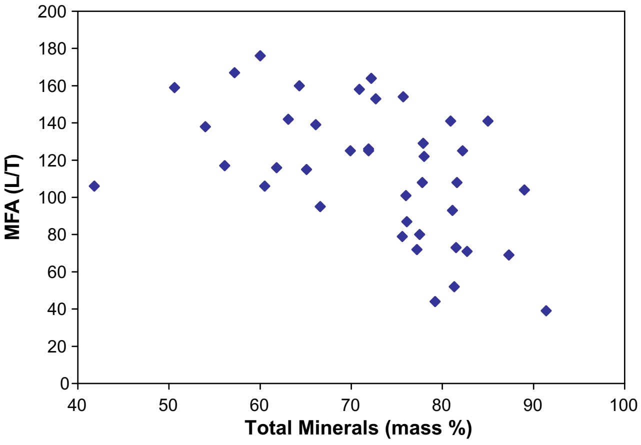

Fig. 5. Variation of total mineral content with MFA content. Although there is no direct relationship, a weak negative correlation is observable due to the fact that increase of MFA (kerogen) percentage means generally less inorganic minerals in oil shale, and vice versa.

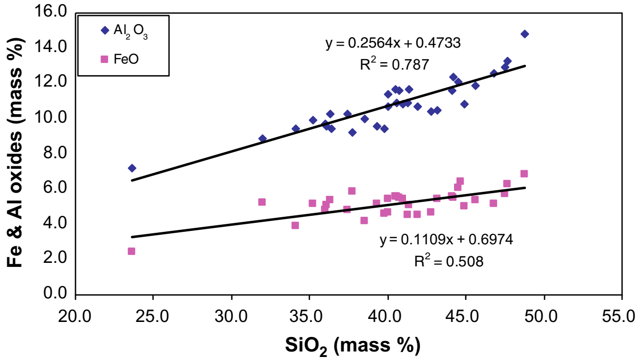

Fig. 6. Plot of Fe and Al oxide contents against silica content showing a positive correlation. See text for details.

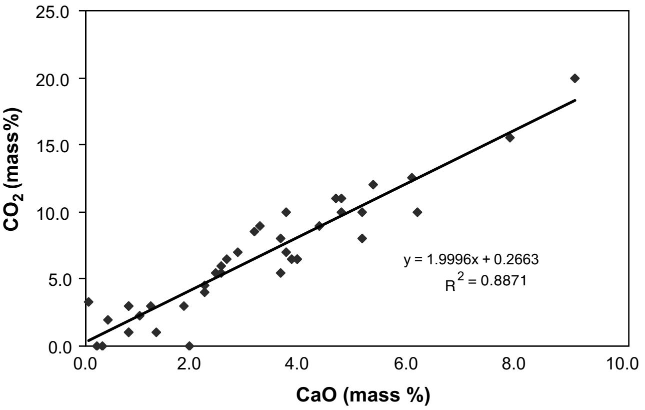

Fig. 7. Correlation of carbon dioxide and Ca oxide content. Note the strong correlation suggesting that carbonates are mainly in the form of $CaCO_3$.

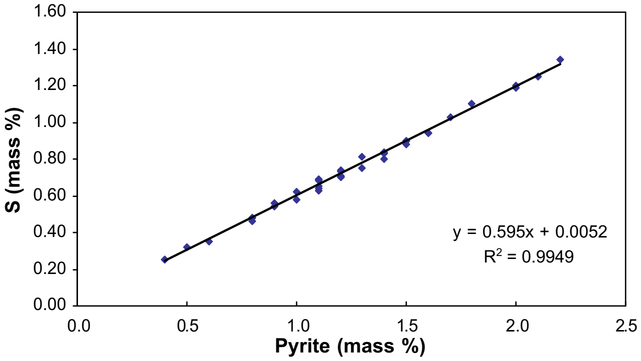

Fig. 8. Correlation of sulphur with pyrite. Very strong positive correlation indicates that almost all sulphur in oil shale come from pyrite.

(quartz) varieties. In addition, pyrite and other iron oxide minerals contribute to the deviation in silica and iron oxide correlation, driving the linear regression value even lower. In Figs. 1a and 2d, it is apparent that there are varying amounts of quartz in these samples.

Total carbon represents the summed amount of organic carbon and inorganic carbon. The main source of organic carbon is kerogen while that of inorganic carbon is carbonate. Most carbonate exists as calcium or magnesium carbonates, although some samples have considerable amounts of siderite. This is evident in the strong correlation of Ca and CO_2 contents in Fig. 7.

As shown in Fig. 8, average sulphur content of these rocks is below 1% making it compatible with other low-sulphur oil shales around the world. Sulphur in fuel is a major environmental concern. It is therefore of interest to find the source of sulphur in oil shale. Sulphur can come from many sources and in many forms. However, the very strong positive correlation shown in Fig. 8 indicates that the major source of sulphur in this oil shale is pyrite. As shown in Fig. 1 F, pyrite is distributed rather evenly and randomly throughout the oil shale. This information may be used in understanding the chemistry in retorting oil shales. Since pyrite is the only significant source of sulphur in the oil shale, removal of pyrite from oil shale prior to retorting can reduce the sulphur content in the shale oil to almost zero. This will not only improve the quality of the oil, but also reduce the refinery processing costs down the line. Although there are currently no industrial processes to remove pyrite from oil shale, it may be possible to do so with a simple physical method, since pyrite is the densest mineral in oil shale and has strong paramagnetic properties.

4. Conclusions

Mineralogical and geochemical results indicate that there are no significant trends in mineralogy with sampling depth for the tertiary oil shales discussed here. Different types of clays, quartz and feldspar contents vary independently. This observation suggests that the oil shales in consideration had not undergone any meteoric weathering or alterations.

Organic carbon content and hydrogen content is strongly correlated, indicating that almost all organic carbon occurs as kerogen. Kerogen content varies between 7.6% and 29%.

It was found that all the sulphur comes from pyrite, and if a simple process can be designed to remove sulphur prior to retorting of oil shale, it will vastly improve the quality of the shale oil and significantly reduce the refining cost.

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References

[1] Regtop RA, Ellis J, Crisp PT, Ekstrom A, Fookes CJR. Pyrolysis of model compounds on spent oil shales, minerals and charcoal. Fuel 1985;64:1640–6.
[2] Schmidt SJ. New directions for shale oil: Path to a secure new oil supply well into this century [on the example of Australia]. Oil Shale 2003;20(3):333–46 [special issue].
[3] Dyni JR. Geology and resources of some world oil-shale deposits: US Geological Survey Scientific Investigations Report 2005-5294, 2006;42 p.
[4] Kattai V, Lokk U. Historical review of the kukersite oil shale exploration in Estonia. Oil Shale 1998;15(2):102–10.
[5] Pierce BS, Warwick PD, Landis ER. Assessment of the solid fuel resource potential of Armenia. U.S. Geological Survey Open-file report: 94-149. 1994:88 p.
[6] Regtop RA, Crisp PT, Ellis J. Chemical characterization of shale oil from Rundle, Queensland. Fuel 1982;61(2):185–92.
[7] Bhargava S, Awaja F, Subasinghe ND. Characterisation of some Australian oil shale using thermal, X-ray and IR techniques. Fuel 2005;84:707–15.
[8] Patterson JH, Lindner AW. Inorganic geochemistry and mineralogy of Unit B, Duaringa oil shale deposit. Fuel 1990;69(9):1081–5.
[9] Patterson JH, Henstridge DA. Comparison of the mineralogy and geochemistry of the Kerosene Creek Member, Rundle and Stuart oil shale deposits, Queensland, Australia. Chemical Geology 1990;82:319–39.
[10] Slansky E. Minerals in some Australian oil shales. Fuel 1983;62:469–71.
[11] Berkovich AJ, Young BR, Ray A, Schmidt SJ. The effect of minerals on retorting enthalphies of some Australian Tertiary oil shales. Fuel 1998;77(9/10):987–93.

[12] Subasinghe ND, Akolekar DB, Bhargava SK. Study of mineral reactions of oil shale under different environmental conditions using in-situ hot-stage XRD analyses. Dev Chem Eng Mineral Process 2006:277–86.

[13] Al-Otoom AY, Shawabkeh RA, Al-Harahsheh AM, Shawaqfeh AT. The chemistry of minerals obtained from the combustion of Jordanian oil shale. Energy 2005;30:611–9.

[14] Arro H, Prikk A, Pihu T. Calculation of qualitative and quantitative composition of Estonian oil shale and its combustion products. Part 1. Calculation on the basis of heating value. Fuel 2003;82:2179–95.

[15] Berkovich AJ, Levy JH, Schmidt SJ, Young BR. Heat capacities and enthalpies for some Australian oil shales from non-isothermal modulated DSC. Thermochimica Acta 2000;357/358:41–5.

[16] Patterson JH. A review of the effects of minerals in processing of Australian oil shales. Fuel 1994;73(3):321–7.

[17] Boreham CJ, Powell TG, Hutton AC. Chemical and petrographic characterization of the Australian Tertiary Duaringa oil shale deposit. Fuel 1988;67:1369–77.

[18] Brons G, Siskin M, Botto RI, Guven N. Quantitative mineral distributions in Green River and Rundle oil shales. Energy & Fuels 1989;3:85–8.

[19] Subasinghe ND. Formation of a phosphate deposit through weathering and diagenesis – an example from Sri Lanka. Ph.D. Thesis (Unpubl.) Univ. of Reading, UK.1998;p 301.